ATIP Report: Nanocarbons for Battery Applications in China

ATIP/China

ABSTRACT: Motivated by the rapid development of portable electronics, electric vehicles (EVs), and renewable energy harvesting, advanced materials with exceptional electrical, thermal, chemical, and mechanical properties for energy storage devices featuring good flexibility, high power and energy densities, and low cost are highly sought after. With the rapid growth of nanotechnology (nanotech), two typical types of nanocarbon materials of recent interest in electrochemistry - namely, carbon nanotubes (CNTs) and graphene - have displayed great potential for improving the existing or even further developing high-performance batteries. This report presents the current status of research on CNTs and graphene for advanced lithium battery (LIB) applications in China, primarily focusing on the relevant government programs as well as the leading players in academia and important research advancements. An analysis of publications is presented and the challenges of developments in this area are also briefly discussed.

KEYWORDS: Advanced Materials, Carbon Nanotubes / CNT, Chemistry, Energy / Power / Natural Resources, Government S&T Policy / Funding, MEMS / Nanotechnology / NEMS, Physics

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14. ABSTRACT
Motivated by the rapid development of portable electronics, electric vehicles (EVs), and renewable energy harvesting, advanced materials with exceptional electrical, thermal chemical, and mechanical properties for energy storage devices featuring good flexibility, high power and energy densities, and low cost are highly sought after. With the rapid growth of nanotechnology (nanotech), two typical types of nanocarbon materials of recent interest in electrochemistry - namely, carbon nanotubes (CNTs) and graphene - have displayed great potential for improving the existing or even further developing high-performance batteries. This report presents the current status of research on CNTs and graphene for advanced lithium battery (LIB) applications in China, primarily focusing on the relevant government programs as well as the leading players in academia and important research advancements. An analysis of publications is presented and the challenges of developments in this area are also briefly discussed.

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EXECUTIVE SUMMARY

- In the past decade, basic research on carbon nanotubes (CNTs) and graphene in China has been vigorously funded by both the central and local governments as well as industries, with totals reaching hundreds of millions of United States Dollars (US$). Within this funding area, CNTs and graphene-based electrochemical applications, particularly in batteries, is one of the priority research subjects that have been strongly supported.
- The number of publications on nanocarbons in China has maintained steady growth since 1995, with a particularly sharp increase within the past four years. In terms of the number of paper citations, China has currently overtaken Japan and the United Kingdom (UK), but still lags far behind the US. However, this gap has been narrowing significantly over the past few years.
- There are presently about 15-25 domestic research groups leading in the synthesis and application of either CNTs, graphene, or both. The numbers of key researchers engaged in the area of graphene currently outnumber those in the CNT area. About one-third of these leading groups have identified nanocarbon research for battery applications as one of their most important research interests or directions. Institutes of the Chinese Academy of Sciences (CAS) and Tsinghua University are presently the top research organizations playing critical roles in the relevant fields in China.
- Chinese researchers have comprehensively investigated the potential of CNT and graphene for electrode applications in energy storage batteries due to the many useful properties of these materials. Recent achievements by Chinese researchers have been concentrated on developing composite electrode materials and conductive additives in lithium-ion batteries (LIBs) and composite cathodes in novel lithium-sulfur (Li-S) and lithium-oxygen (Li-Air) batteries.

IMPACT & ASSESSMENT

It is rare in the history of modern science for a single topic area to be so productive for both fundamental research and practical applications as the field of nanocarbon materials has been. Several breakthrough discoveries in the synthesis and fabrication of these materials with unique properties, such as CNTs and graphene, during the last few decades have greatly inspired a number of Chinese scientists and engineers engaged in the energy storage field. As a result, Chinese researchers have made rapid progress in the relevant topic areas, with an increasing academic influence around the world. ATIP found that even

in the US, many outstanding achievements in this field have been made by Chinese-American scientists, who are often in cooperation with Chinese teams in China. As such China's role should not be ignored in this international research frontier where the competition is currently very stiff.

1. INTRODUCTION

The era of nanocarbon materials has started, with the first reports on fullerenes and related compounds coming out in the mid-eighties. A tremendous increase of research activity has been observed in this field ever since, resulting in a rapid growth of the family of nanocarbon materials. In the last two decades, one-dimensional (1D) and two-dimensional (2D) nanocarbon materials such as carbon nanotubes (CNTs) and graphene have attracted significant attention from the scientific community due to their unique electronic, optical, thermal, mechanical, and chemical properties. By virtue of their advantageous properties, the use of CNTs, graphene, and their nanohybrids in energy applications have been extensively researched worldwide to further improve the performance of batteries. As an important and urgent research frontier that has been attracting unprecedented attention from global academia, the numbers of publications in this field have been increasing rapidly. Many of the leading countries in the fields of material science and nanoscience, such as the United Status (US), United Kingdom (UK), and Japan, etc. have launched relevant national research and development (R&D) projects with heavy funding, with an interest in taking the leading position. Inspiring results from laboratories have appeared frequently in the top relevant international journals in recent years. Meanwhile, academic competition in this area around the world also appears to be becoming increasingly stiff, as the original results are quickly replaced or updated with new emerging ones. Nevertheless, to date, any mass use of CNTs and graphene in commercialized batteries is not prevalent in the market yet, primarily due to the relatively high cost and low technological stability and controllability associated with large-scale use.

R&D of nanocarbon materials in China started in the late 1980s. According to Prof. Huiming CHENG at the Institute of Metal Research (IMR), Chinese Academy of Sciences (CAS), the relevant study has become one of the most active and fruitful research areas in China, with a considerable R&D budget devoted by both central and local governments as well as industries for decades. So far, China has established its internationally recognized reputation in the synthesis of nanocarbon materials, as well as a leading position in large-scale production for industry, which to some extent lays a solid foundation for nanocarbon-based research aimed at battery applications.

**Note: This report uses a foreign currency conversion rate of 1 Chinese Yuan Renminbi (RMB) = .163 United States Dollar (US$).*

2. GOVERNMENT PROGRAMS

In the past decade, basic research on CNTs and graphene in China has been vigorously funded by a number of central government funding agencies, represented by the Ministry of Science and Technology (MOST), CAS, National Natural Science Foundation of China (NSFC), etc. At the same time, some local governments and domestic companies are also allocating special funds to support relevant research. According to Prof. CHENG's rough statistics, the number of granted programs funded by MOST, CAS and NSFC in this topic area has exceeded 1,500, with R&D funding totaling more than US$200 million during China's National 11th and

12th Five-Year plan periods (from 2006-2015). Local governments and industries have invested additional R&D funding exceeding US$100 million during the same period. Among these granted projects, CNT- and graphene-based electrochemical applications, particularly in batteries, is one of the priority research subject areas that has been strongly funded under MOST's Major Research Plan, National Basic Research Program (973 Program), and National High-Tech R&D Program (863 Program) as well as the CAS Innovation Programs and Strategic Priority Research Program and various programs of NSFC. Tables 1 and 2 below provide an introduction to some of the main central government programs, based on the available data from the past decade.

Table 1. Main Programs Funded by MOST's Major Research Plan and 973 Program (2006-2015)

Program Term	Program Title	Funding*	Chief Scientist	Affiliation	Funding Type
2006-2010	Exploring research on structural control, growth mechanisms and application of CNTs	~RMB 14.4 million	Huiming CHENG	Institute of Metal Research (IMR), CAS	Major Research Plan
1/2011 - 8/2015	Research on key technology of CNT controllable preparation and large-scale application	~RMB 23.3 million			
7/2007 - 8/2011	Basic research on preparation, characterization of nanohybrid energy materials and the application in lithium secondary battery	RMB 19 million	Liquan CHEN	Institute of Physics (IoP), CAS	Major Research Plan
1/2009 - 8/2013	Basic research on new secondary battery and its related energy materials	~RMB 49.8 million	Feng WU	Beijing Institute of Technology (BIT)	973 Program
2015-2019	Basic research on new high-performance secondary battery	~RMB 15.9 million for the first two years; N/A for the last three years			
9/2010 - 9/2015	Basic research on application of nanomaterials and technology in secondary battery for smart grid storage	~RMB 11.6 million for the first two years; N/A for the last three years	Jun CHEN	Nankai University	Major Research Plan
1/2011 - 8/2015	Research on controllable preparation, property of graphene and graphene-based device	~RMB 23.6 million	Xiaolong CHEN	IOP, CAS	Major Research Plan
2013-2017	Basic research on new 3D nanostructural based lithium secondary storage battery	~RMB 23.4 million	Shichao ZHANG	Beihang University	Major Research Plan
2013-2017	Design and control of functional meso-porous materials for efficient energy use	~RMB 22.8 million	Yi TANG	Fudan University	Major Research Plan
2013-2017	Basic research on nano-scale preparation of key materials for solid-state lithium battery featuring safety, light mass and high efficiency	~RMB 4.8 million	Chuhong ZHANG	Sichuan University	Major Research Plan
2014-2018	Design and control of nanomaterials for high-efficiency energy conversion and storage of secondary lithium air battery	~RMB 7 million for the first two years; N/A for the last three years	Haoshen ZHOU	Nanjing University	Major Research Plan

Program Term	Program Title	Funding*	Chief Scientist	Affiliation	Funding Type
2014-2018	Design and preparation of micro/nano superstructural carbon materials and their high-efficiency energy conversion and storage research	~RMB 7.1 million for the first two years; N/A for the last three years	Feiyu KANG	Tsinghua University (Shenzhen Campus)	Major Research Plan
2015-2019	Basic research on flexible nanomaterials of energy storage	~RMB 2.3 million for the first two years; N/A for the last three years	Huiwu	Tsinghua University	Major Research Plan

**Note: 1 Chinese Yuan Renminbi (RMB) = ~US$0.163*

Table 2. Main Programs Funded by NSFC

<table>
<tr><th>Program Term</th><th>Program Title</th><th>Funding*</th><th>Chief Scientist</th><th>Affiliation</th><th>Funding Type</th></tr>
<tr><td>1/2007 - 12/2010</td><td>Research on high-performance carbon materials</td><td>RMB 2.0 million</td><td>Yali LI</td><td>Tianjin University</td><td>Funds for Distinguished Young Scholars</td></tr>
<tr><td>1/2010 - 12/2012</td><td rowspan="2">Exploring research on controllable preparation, structure of nanocarbon materials and their application</td><td>RMB 5 million</td><td rowspan="2">Huiming CHENG</td><td rowspan="2">IMR, CAS</td><td rowspan="2">Funds for Innovative Research Groups</td></tr>
<tr><td>1/2013 - 12/2015</td><td>RMB 6 million</td></tr>
<tr><td>1/2012 - 12/2014</td><td>Research on graphene-based new energy materials</td><td>RMB 1.0 million</td><td>Gaoquan SHI</td><td>Tsinghua University</td><td>Major International (Regional) Joint Research Project (NSFC-NSF, Sino-US)</td></tr>
<tr><td>1/2013 - 12/2016</td><td>Applied basic research on aligned CNTs/Polymer composites for energy use</td><td>RMB 2.0 million</td><td>Huisheng PENG</td><td>Fudan University</td><td>Funds for Distinguished Young Scholars</td></tr>
<tr><td>1/2013 - 12/2016</td><td>Research on energy conversion and storage materials</td><td>RMB 2.0 million</td><td>Yuguo GUO</td><td>Institute of Chemistry (IOC), CAS</td><td>Funds for Distinguished Young Scholars</td></tr>
<tr><td>1/2013 - 12/2017</td><td>Research on controllable preparation method of 2D atomic crystal and its functional application</td><td>~RMB 3.8 million</td><td>Wencai REN</td><td>IMR, CAS</td><td>Major Program</td></tr>
<tr><td>1/2013 - 12/2017</td><td>Functional control and mechanism research on nanocarbon materials of energy storage</td><td>RMB 3.1 million</td><td>Feiyu KANG</td><td>Tsinghua University (Shenzhen Campus)</td><td>Key Program</td></tr>
</table>

Program Term	Program Title	Funding*	Chief Scientist	Affiliation	Funding Type
2013.1-2017.12	Controllable growth and property research on graphene-based nanomaterials	RMB 2.8 million	Hongjun GAO	IOP, CAS	Major International (Regional) Joint Research Project (NSFC-NSF, Sino-US)
1/2014 - 12/2017	Research on 2D carbon materials	RMB 2.0 million	Wencai REN	IMR, CAS	Funds for Distinguished Young Scholars
1/2014 - 12/2017	Research on functional nanocarbon materials and their application	RMB 2.0 million	Anyuan CAO	Peking University	Funds for Distinguished Young Scholars
1/2014 - 12/2017	Research on low-dimensional conjugated nanocarbon structure and functionality	RMB 2.0 million	Liangti QU	BIT	Funds for Distinguished Young Scholars
1/2014 - 12/2017	Controllable preparation of key materials for high-energy-density Li-S battery and structure-activity relationship research	RMB 2.6 million	Yuezhong MENG	Sun Yat-sen University	Major International (Regional) Joint Research Project (NSFC-Guangdong NSF)
1/2014 - 12/2018	Graphene-based electrode design for electrochemical storage system and its engineering fundamental research in manufacturing process	RMB 3.0 million	Zifeng MA	Shanghai Jiaotong University (SJTU)	Key Program
1/2015 - 12/2017	Research on multilevel carbon materials	RMB1.0 million	Qiang ZHANG	Tsinghua University	Funds for Excellent Young Scholars
1/2015 - 12/2019	CNT controllable growth and toughening mechanism study in C/C composite preforms	RMB 3.6 million	Hejun LI	Northwestern Polytechnical University (NPU)	Key Program
1/2015 - 12/2019	Research on graphene modified new type of lightweight rare earth intermetallic compounds and their high capacity storage feature	RMB 3.5 million	Xingguo LI	Peking University (PKU)	Key Program

**Note: 1 Chinese Yuan Renminbi (RMB) = ~US$0.163*

It should also be noted that two important projects funded by local governments on nanocarbon-related research and applications will possibly be initiated sometime this year, according to Prof. CHENG. The Beijing government plans to invest a total of US$160 million

into the project from 2015-2020, and the chief scientist undertaking the project is probably Prof. Zhongfan LIU at Peking University. Meanwhile, the Liaoning government will also invest US$16 million in relevant fields for the period 2015-2017. However, at the time of this writing, the corresponding funding plans had not been officially announced nor confirmed.

3. RESEARCH STATUS

3.1 Paper Analysis

The number of publications on nanocarbons in China has been maintaining steady growth since 1995, which a particularly sharp increase within the past four years. The number of papers published in 2014 reached about 11,000, and this year the total will probably exceed 12,000 papers (see Figure 1 below).

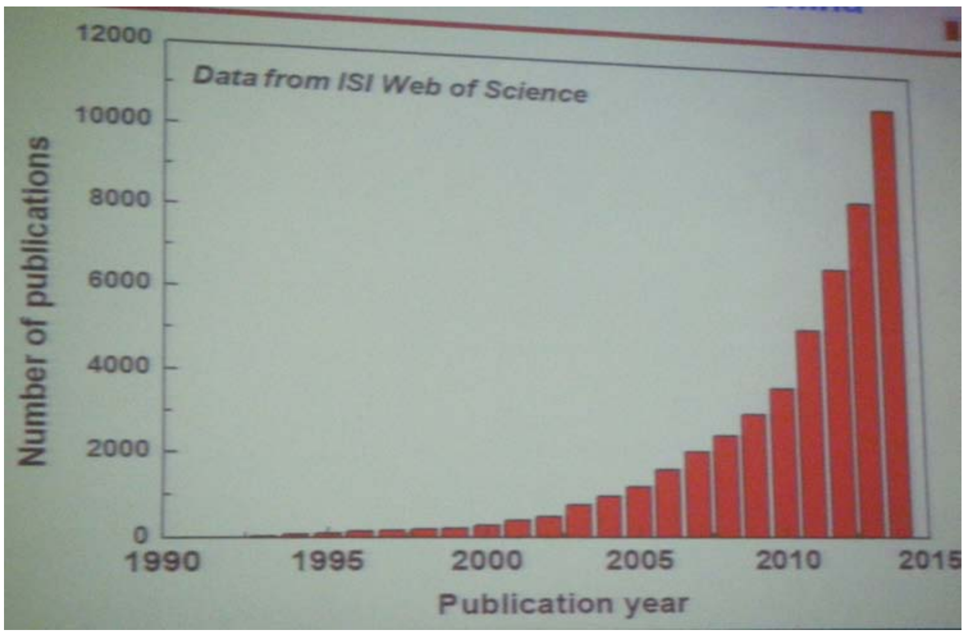

Figure 1. Number of publications on the topic of nanocarbons in China since 1990

According to data from the ISI Web of Sciences, the total number of publications in relevant fields from China for the period 1985-2014 has exceeded those from some leading countries such as the US, Japan, and the UK (see Figure 2 below). Meanwhile in terms of the number of paper citations, China has currently overtaken Japan and the UK, but still lags far behind US, but the gap has been narrowing significantly over the past few years. For instance, in 2013 the average number of paper citations from China was about seven, while the US still ranked #1 with a slight advantage of around eight.

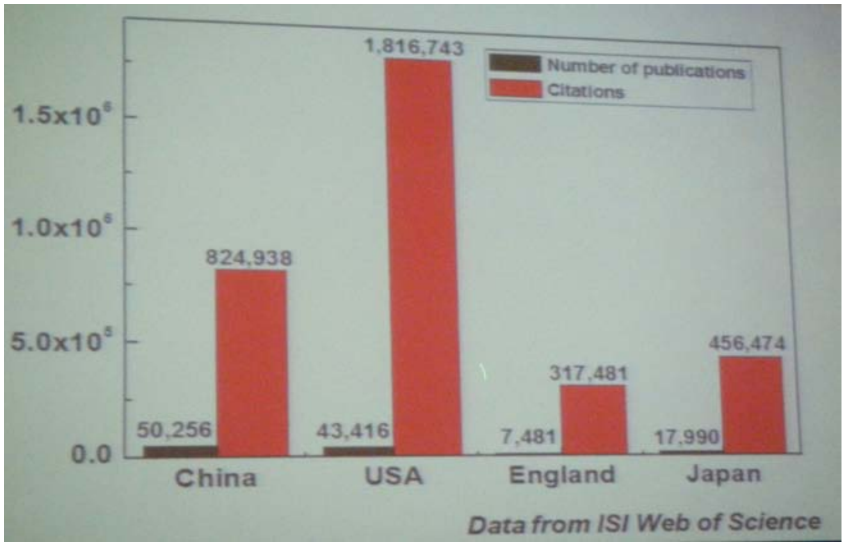

Figure 2. Comparison of total number of publications and citations for China, the US, the UK (England) and Japan for the period 1985-2014

Recent data from the ISI Web of Science also indicate that there are more than 100 domestic universities and research institutes engaged in the field of nanocarbon research in China. The top ten of these organizations in terms of numbers of publications are presented in Figure 3 below. Since CAS consists of numerous separate institutes, it tops the list with a distinct advantage in the number of publications - over four times more than the second player, Tsinghua University.

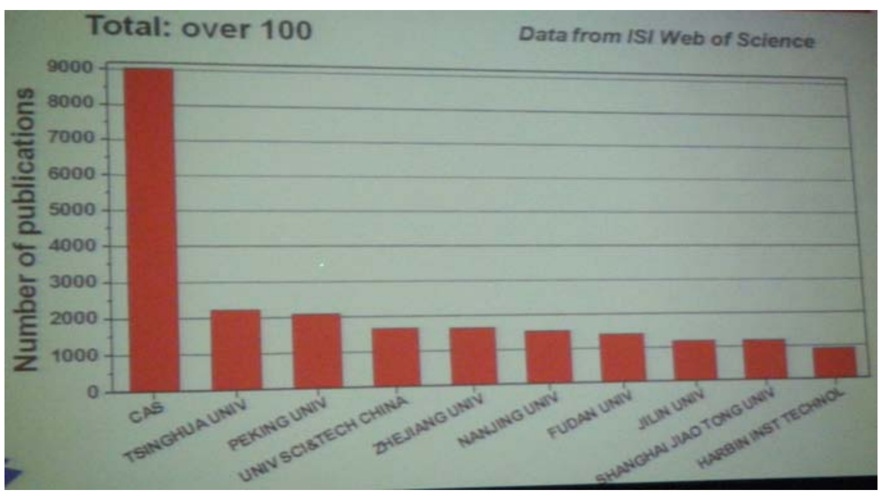

Figure 3. Top ten research institutions conducting research on nanocarbons in China

3.2 Leading Groups

According to Prof. CHENG, there are presently about 15-20 domestic research groups leading in the synthesis and application of CNTs, while five to 10 more key players are engaged in graphene-related research nationwide, compared to those working in the field of CNTs. In particular, some of the leading groups, represented by Prof. CHENG, are

important contributors in both fields. Among them, research on nanocarbon applications in batteries has been identified by a number of groups as one of their most important research interests or directions. Table 3 below presents a list of representatives for these groups, along with a brief introduction of their background in research.

Table 3. Representative Groups in China Working on Nanocarbon Research for Battery Applications

Chief Researchers	Affiliations	Remarks
Huiming CHENG and Feng LI	Advanced Carbon Division of IMR, CAS	CHENG is an academician of CAS and highly recognized for his contributions to high-quality CNTs and large-scale preparations of graphene
Meizhen QU	Chengdu Institute of Organic Chemistry (CIOC), CAS	China's pioneer in CNT continuous batch production and its industrial application in lithium-ion batteries (LIBs)
Fei WEI	Tsinghua University	One of the key contributors in China to realize mass industrial production of CNTs and their application in energy storage systems
Zhaoping LIU	Advanced Li-ion Battery Engineering Lab of Ningbo Institute of Industrial Technology, CAS (CNITECH)	China's pioneer in the mass production of graphene and its industrial application in LIBs
Gaoquan SHI	Tsinghua University	Domestic leading researcher engaged in graphene-based energy conversion and storage devices
Jinghong LI	Tsinghua University	Domestic leading researcher engaged in graphene-based electrochemical applications

3.3 Research Advancements

Chinese researchers have investigated nanocarbon materials such as CNTs and graphene comprehensively as part of electrode technology development for applications in energy storage batteries because of their many useful properties. This section presents some of the recent achievements that have been made in the application of CNTs and graphene, particularly in respect to composite electrode materials and conductive additives in LIBs and composite cathodes in novel Li-S and Li-Air batteries.

3.3.1 As Composite Electrode Materials in Lithium-Ion Batteries (LIBs)

3.3.1.1 Carbon Nanotubes (CNTs)

It has been demonstrated that the electrochemical performance of batteries can be effectively improved by using CNTs as a conductive structure integrated with some existing electrode materials, so Chinese researchers have been paying close attention to synthesis methods for CNT-based electrode composites with high qualities. For example:

1. Researchers from Nanjing University of Science and Technology (NUST) synthesized $LiMn_2O_4$/CNT nanocomposite using a one-step hydrothermal treatment within five

hours. Results show that ultrafine $LiMn_2O_4$ nanoparticles in the range of 10-20 nm are uniformly distributed in the CNT matrix in the nanocomposite, which exhibits excellent cycling stability and rate capability as a cathode for LIBs (over 1000 cycles at 10 C.

2. Prof. CHENG's team at IMR, CAS prepared a high-quality CNT/$Li_4Ti_5O_{12}$ electrode and CNT/$LiFePO_4$ electrode with some kind of *in situ* grinding method that has been granted a patent license in China. The former one can achieve an energy density of 143 mAh/g at 10C and 146 mAh/g at 5C after 300 cycles with 99.9% capacity retention, while the latter one can achieve 100 mAh/g even at 50C.

3. Researchers from Tsinghua University developed a new method where a uniform Fe_3O_4 sheath is magnetron-sputtered onto aligned CNT scaffolds that are directly drawn from CNT arrays. The Fe_3O_4-CNT composite electrode with Fe_3O_4 particles confined to a size of 5-7 nm, exhibits a high reversible capacity of 836 mAh/g at 1C after 100 cycles. As Fe_3O_4 is inexpensive and environmentally friendly, and the synthesis of Fe_3O_4-CNT is free of chemical wastes, researchers believe this composite anode material holds considerable promise for high-performance LIBs.

4. Prof. Feng LI's team at IMR, CAS prepared octahedral Co_3O_4 particles threaded by ultra-long multi-walled CNT (MWCNT) arrays using a hydrothermal process and subsequent calcinations. Experimental results show that the composite can be used as an integrated anode for LIBs without any other additives (such as conductive additives and polymer binders), which exhibits a high reversible capacity of 725 mAh/g at 1C and excellent cyclic stability without capacity degradation after more than 100 cycles at 5C.

3.3.1.2 Graphene

With the technological development of facile, low-cost, and large-scale production of graphene, graphene-based electrode composites for LIBs have been widely studied by Chinese researchers, covering both anodes such as Si, Ge, Sn, etc. and cathode active materials such as $LiFePO_4$, $LiMn_2O_4$, etc. For example:

1. Researchers from IOC, CAS developed Ge@C core-shell nanostructures and reduced graphene oxide (RGO) networks to improve the electrode performance of Ge. The as-synthesized Ge@C/RGO nanocomposite showed excellent cycling performance and rate capability (940 mAh/g at 0.5C after 50 cycles) in comparison with Ge@C nanoparticles (490 mAh/g under the same condition) when used as an anode material for LIBs.

2. Researchers from Shanghai Institute of Ceramics, CAS developed flexible, free-standing, hollow Fe_3O_4/graphene films through vacuum filtration and thermal reduction processes in which graphene formed a 3D conductive network, with hollow and porous Fe_3O_4 spindles being captured and distributed homogeneously. Using the films as binder-free and freestanding electrodes for LIB, a new electrode with 39.6 wt% graphene exhibited a high specific capacity (1555 mAh/g at 1C), enhanced rate capability, and excellent cyclic stability (940 and 660 mAh/g at 2C and 5C after 50 cycles, respectively).

3. Researchers from Fudan University synthesized graphene-wrapped $LiFePO_4$/C composites as cathode materials for LIBs using a rapid, one-pot, microwave-assisted hydrothermal method within 15 minutes at a temperature of 200°C, followed by

sintering at 600°C for two hours under a H_2/Ar atmosphere. Experimental results showed a discharge capacity of 165 mAh/g at 0.1C and 88 mAh/g at 10C, respectively.

4. Researchers from Shandong University prepared a $LiMn_2O_4$/Graphene composite as a cathode material for LIBs via ultrasonic agitation. Experimental results showed reversible capacity of 107 mAh/g at 50C.

3.3.1.3 Graphene-CNT Hybrid

Recent studies have further shown that graphene-CNT hybrid composites have more potential for improving the electrochemical performance of energy storage systems. Recognizing the benefit of graphene-CNTs composite structures, several studies also focused on the synthesis and assembly of these hybrid nanostructures as composite electrode materials in LIBs. For example:

1. Prof. QU's team at CIOC, CAS prepared a composite of graphene oxide sheets, CNTs, and commercial graphite particles used as a high-capacity and binder-free anode material for LIBs. Experimental results showed that this novel composite had a very high reversible Li-storage capacity of 1172.5 mAh/g at current density of 186 mA/g, which is thrice that of the existing commercial graphite anode. The composite also exceeded the theoretical sum of capacities of the three ingredients. More importantly, its reversible capacity below 0.25 V can reach up to 600 mAh/g.
2. Researchers from Nanjing University of Aeronautics and Astronautics (NUAA) synthesized a Ge-graphene-CNT nanostructure using germanium nanoparticles anchored on reduced graphene oxide (Ge-RGO) intertwined with CNT as a composite anode for LIBs. According to the experimental results, the designed anode exhibited an outstanding energy capacity up to 863.8 mAh/g at 1C after 100 cycles and good rate performances of 1181.7, 1073.8, 1005.2, 872.0, 767.6, and 644.8 mAh/g at 1C, 2C, 4C, 8C, 16C, and 32C, respectively.

3.3.2 As Conductive Additives in Lithium-Ion Batteries (LIBs)

The commercial production capacity of CNT powders in China is over 1000 tons per year (T/y), while the capacity for graphene sheets is about 500 T/y. According to Prof. WEI at Tsinghua University, the majority of nanocarbon powder is presently being used in LIBs as a conductive additive/filler to try to replace conducting carbon black in China. Taking account of its significant market value, a number of relevant basic research projects have been conducted by Chinese researchers. For example:

1. Researchers from BIT developed a commercialized $LiFePO_4$-based LIB using CNT and conductive carbon black as conductive additives. The experimental results showed that the battery had only 1.0 mΩ resistance with a specific capacity of 146.32 mAh/g at 0.5C by using the new compound additives - better than the one with conventional conductive additives (3.25 mΩ resistance with 139.06 mAh/g under the same conditions).
2. Researchers from Tianjin University and Tsinghua University used flexible and planar graphene conductive additives for LIBs. Results showed that with a much lower fraction of graphene additives (2 wt%) than those of commercial carbon-based additives (20 wt%), the graphene-introduced $LiFePO_4$ cathode shows a better charge/discharge performance than commercial cases.

3. Researchers from Chongqing University made the comparison of carbon conductive additives with different dimensions, including carbon black, MWCNTs, and graphene sheets on the electrochemical performance of $LiFePO_4$ cathodes. The experimental results indicated that $LiFePO_4$ mixed with graphene nanosheets exhibited the best electrochemical performance, of which the specific capacity was up to 146 mAh/g at 0.1C and 125 mAh/g at 1C.

3.3.3 As Composite Cathodes in Lithium-Sulfur (Li-S) Batteries

3.3.6.1 CNTs/Sulfur Composites

Chinese researchers find Li-S batteries with a high theoretical capacity to be a very attractive target. However, the commercial use of Li-S batteries still faces obstacles such as the low electrical conductivity of sulfur and lithium sulfide and the dissolution of polysulfides. The introduction of CNTs into Li-S batteries sheds light on the efficient use of sulfur by improving the conductivity of the composites and restraining the shuttle effect of polysulfides. This is an area where Chinese researchers have made important contributions in recent years. For example:

1. Prof. WEI's team at Tsinghua University employed CNTs to build the unblocked conductive skeleton. They obtained CNTs/sulfur composites as a cathode with high sulfur content of 90% via a room-temperature, one-step ball-milling treatment of aligned CNTs and sulfur. The experimental results exhibited a superior density of 1.98 g /cm^3 (2.07 g/cm^3 for sulfur), which will greatly increase the volumetric energy density of the Li-S battery. Moreover, WEI et al. developed a facile way to tune the shuttle of polysulfide by matching the sulfur/electrode loading. Based on that method with CNTs/Sulfur cathode, they developed a Li-S cell with a high initial discharge capacity of 1053 mAh/g at 1C and an ultralow decay rate of 0.049% per cycle during 1000 cycles.
2. Researchers from Ningbo Institute of Material Technology and Engineering (NIMTE) of CAS prepared a flexible composite film composed of CNTs and sulfur as the cathode for an Li-S battery through a simple two-step heating process with a high energy density of ~1200Wh/kg based on the total mass of the electrode. Experimental results showed that the film electrode delivers an initial capacity of 1100 mAh/g and can retain a reversible capacity of 740 mAh/g after 100 cycles at 0.1C. Good rate capability with a reversible capacity of 520 mAh/g can also be reached at the rate of 2C.
3. Researchers at Tsinghua University fabricated a binder-free CNT/sulfur composite material featured by clusters of sulfur nanocrystals anchored across the superaligned CNT (SACNT) matrix via a facile solution-based method. Experimental results showed that the cathode delivers an initial discharge capacity of 1071 mAh/g, a peak capacity of 1088 mAh/g, and capacity retention of 85% after 100 cycles with high Coulombic efficiency (~100%) at 1C. Moreover, at high current rates the composite displays impressive capacities of 1006 mAh/g at 2C, 960 mAh/g at 5C, and 879 mAh/g at 10C.

3.3.6.2 Graphene-based Materials/Sulfur Composites

Similar to CNT/sulfur composites, sulfur-graphene composites also show promising results that could lead to improved Li-S battery stability and efficiency. Chinese researchers are very active in the relevant areas and are thereby publishing many important results. For example:

1. Researchers from the Institute of Ceramics, CAS developed a Scotch-tape-like sulfur-graphene cathode. The unique structure containing 73 wt% sulfur exhibited good overall electrochemical properties of 615 mAh/g at the current density of 1675 mA/g after 100 cycles and 570 mAh/g at the current density of 3350 mA/g; (2) Prof. CHENG's team at the CAS Institute of Metal Research (IMR) developed a graphene/sulfur sandwich structure with pure sulfur between two graphene membranes. One graphene membrane was used as a current collector with sulfur coated on it as the active material, and the other one was coated on a commercial polymer separator. Experimental results showed that capacities of 1000 mAh/g and 750 mAh/g can still respectively be achieved, even at the current density of 1.5A/g and 6A/g for an Li-S battery with such a unique configuration.

2. Prof. SHI's team at Tsinghua University developed a reduced graphene oxide (rGO)-sulfur composite aerogel with a compact self-assembled rGO skin which was further modified by an atomic layer deposition (ALD) of ZnO or MgO layer, and used as a free-standing electrode material of a Li-S battery. According to the experimental results ZnO modified G-S electrode with 55 wt% sulfur loading delivered a maximum discharge capacity of 998 mAh/g at 0.2C and a capacity of 846 mAh/g was achieved after charging/discharging for 100 cycles with a coulombic efficiency higher than 92%. When they used $LiNO_3$ as a shuttle inhibitor, the composite electrode showed an initial discharge capacity of 796 mAh/g and capacity retention of 81% after 250 cycles at 1C with an average coulombic efficiency higher than 99.7%.

3.3.6.3 Graphene-CNT Hybrids

Many of the latest research achievements made by Chinese researchers are concentrated in the area of graphene-CNT hybrid materials. For example:

1. Prof. WEI's team at Tsinghua University successfully fabricated sandwich-like nitrogen-doped aligned CNT/graphene (N-ACNT/G) hybrids via a two-step catalytic growth on bifunctional natural materials. When they used this hybrid as the cathode of an Li-S battery, a high initial reversible capacity of 1152 mAh/g becomes available at 1C, maintaining 880 mAh/g after 80 cycles – this is about 65% higher than that of sole aligned CNTs. Even at a high current density of 5C, a reversible capacity of 770 mAh/g can be achieved.

2. Another research team from Tsinghua University also reported the use of super-aligned CNT/graphene (S-CNT/G) hybrid materials as a 3D conducting framework for sulfur accommodation. The CNT network acts as a skeleton to form a self-sustained cathode that is binder-free, highly conductive, and flexible for Li-S batteries. According to the researchers, based on this superior structure, the S-CNT/G nanocomposite achieves a high discharge capacity of 1048 mAh/g at 1C with a capacity fade as low as 0.041% per cycle over 1000 charge-discharge cycles.

3.3.7 As Composite Cathodes in Lithium-Oxygen (Li-Air) Batteries

Exploring the potential applications of nanocarbons in Li-Air batteries is currently a top interest of Chinese researchers, since Li-Air batteries have the potential to be the next big leap in battery technology. However, their development still faces significant challenges. To date, Chinese researchers have done a great deal of work in improving the

performance of Li-Air batteries by using doped/modified CNTs and graphene sheets as the air electrode with a unique structure design. For example:

1. Researchers at Fudan University synthesized binder-free nickel-foam-supported nitrogen-doped CNTs using a floating catalyst chemical vapor deposition (FCCVD) method. Experimental results showed that this material could be employed as the air electrode in Li-Air batteries, and it delivers 1814 mAh/g (normalized to the weight of the air electrode) at a current density of 0.05 mA/cm^2. The researchers also prepared a MnO_2-graphene nanosheet (GNS) composite air electrode by mixing aqueous GNS colloids and aqueous MnO_2 dispersions. According to the experimental results, a capacity of 1500 mAh/g over 30 cycles was achieved using this composite air electrode.
2. Researchers from Wuhan University and Peking University reported an Li-Air battery with a free-standing, highly porous Pd-modified CNT (Pd-CNT) sponge cathode, which was synthesized through a CVD growth followed with an electrochemical deposition process. According to the researchers, the existence of Pd nanoparticles improves the catalytic reactivity of the oxygen reduction reaction. The battery is durable under any humidity level and delivers a capacity as high as 9092 mAh/g.
3. Researchers from Huazhong University of Science and Technology (HUST) hydrothermally-synthesized graphene sponge modified with Fe-N-C catalyst nanoparticles as the cathode for an Li-Air battery. According to the experimental results with dimethyl sulphoxide as electrolyte, the capacity can reach 6762 mAh/g. The battery with this air electrode also exhibits stable cyclic performance and effective reduction of charge potential plateau.

4. CHALLENGES

From a practical point of view, the large-scale synthesis of nanocarbons - especially CNTs and graphene - good characterization and easy handling still present big issues for their real application in the battery industry. Although a number of preparation methods have been developed and their efficiency has been demonstrated, all of them have shown disadvantages in one way or another. For example, high cost is the biggest obstacle associated with using a CVD process, which is by far the dominant method for high-volume production of CNTs and graphene. The price of bulk purified multi-walled CNT (MWCNT) is several times higher than the commercially available carbon fibers. The production cost of graphene is high, because its formation is related to an interface growth mechanism and depends on the underlying substrates such as Cu foil or Ni single crystal, which must subsequently be removed. Furthermore, the shape, size, purity, and crystallographic orientation of nanocarbons - which are important characteristics of the unique properties of nanocarbons - need to be finely controlled for different battery applications. In particular, the dispersion technology for efficient design of hybrid nanocarbon materials needs to be further improved. The present production of nanocarbons depends largely on a number of factors, such as carbon precursors, substrate, catalyst, temperature, condensation and carbonization process, etc. Because of substantial differences in the production procedures, using a general method to assemble nanocarbons that exhibit controllable patterns in ways that are desirable for battery applications remains a challenge.

5. CONCLUSION

Driven by the potentially high demands of China's growing market for EVs, popular wearable electronics, etc., the development of high-capacity and flexible LIBs is currently one of the most important and remarkable research topics for Chinese researchers who are engaged in the R&D and application of nanocarbons, especially in terms of CNTs and graphene. Comprehensive research in Chinese academia has been conducted with support from heavy R&D funding in the relevant fields over the past decade, in a concerted effort to bring China to the global forefront of this field. To date, good investment returns have been achieved in terms of increasing numbers of academic publications and citations as well as fruitful research achievements in the field. However, compared to the boom in academic circles, the relevant engineering applications for advanced batteries have been developing relatively slow in China. Chinese researchers believe at the current stage there are still some issues to be solved, both scientific and technological and non-scientific and technological, before any large-scale application of nanocarbons in the battery industry can occur - particularly in high-end applications such as EVs using power LIBs.

END OF REPORT

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